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A Thermo-Chemical Reactor for analytical atomic spectrometry

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ABSTRACT

A novel atomization/vaporization system for analytical atomic spectrometry is developed. It consists of two electrically and thermally separated parts that can be heated separately. Unlike conventional electrothermal atomizers in which atomization occurs immediately above the vaporization site and at the same instant of time, the proposed system allows analyte atomization via an intermediate stage of fractional condensation as a two stage process: Vaporization→Condensation→Atomization. The condensation step is selective since vaporized matrix constituents are mainly non-condensable gases and leave the system by diffusion while analyte species are trapped on the cold surface of a condenser. This kind of sample distillation keeps all the advantages of traditional electrothermal atomization and allows significant reduction of matrix interferences. Integration into one design a vaporizer, condenser and atomizer gives much more flexibility for in situ sample treatment and thus the system is called a Thermo-Chemical Reactor (TCR).

Details of the design, temperature measurements, vaporization–condensation–atomization mechanisms of various elements in variety of matrices are investigated in the TCR with spectral, temporal and spatial resolution. The ability of the TCR to significantly reduce interferences and to conduct sample pyrolysis at much higher temperatures as compared to conventional electrothermal atomizers is demonstrated. The analytical potential of the system is shown when atomic absorption determination of Cd and Pb in citrus leaves and milk powder without the use of any chemical modification.

1. Introduction

Quantitative knowledge of a substance or material elemental composition is important for practically all aspects of human activities including environmental issues, life sciences, industry, etc. Nowadays, the most prevailing methods for elemental quantification of a substance's chemical composition are provided by analytical atomic spectrometry. All versions of analytical spectrometry: atomic absorption, emission, fluorescence and mass spectrometry can only detect free analyte atoms or ions in the gas phase. Thus, in all the cases the sample under investigation needs to be first converted from the condensed state (solid, liquid) to a cloud of free atoms/ions. Then analyte atoms are detected via their emission, fluorescence, absorption or as ions in a mass spectrometer. High temperature flames, inductively coupled and microwave induced plasmas, arcs and sparks, laser ablation are used as atomizers to convert the sample to be analyzed from the condensed phase into a cloud of free atoms/ions. One of the most popular means of the conversion is electrothermal vaporization/atomization (ETV) of a sample in a tube graphite atomizer. Dozens of thousands ETVs have been manufactured commercially and are used nowadays in most of the laboratories involved into elemental spectrochemical analysis. Operation of all the commercially available atomizers/vaporizers is based on the following one-stage principle:

$$vaporization \rightarrow atomization. \quad (1)$$

That is analyte atomization occurs in a single step immediately above vaporization site and at the same time of vaporization. Thermal pretreatment in these conventional systems typically includes drying and pyrolysis of samples without analyte transfer into the gaseous phase. Despite the widest use of this approach, it is normally plagued by matrix interferences: the analytical signal depends on the type of the substance from which analyte is vaporized. In case of complex matrices, analyte is occluded into the sample matrix crystallines after the pyrolysis step and vaporization kinetics is largely determined by "analyte–matrix" bonds. This results in the fact that the same amount of analyte vaporized from an aqueous standard solution and from a sample may give different analytical signals.

A typical approach to overcome matrix interferences is the use of matrix modifiers that allows analyte stabilization to higher temperatures at which matrix constituents can be removed to a greater extent. A disadvantage of this approach is the necessity of introduction of microgram amount of a modifier and each analyte–matrix combination requires, speaking strictly, its own modifier.

Lots of publications were devoted to investigation of atomization processes in a graphite furnace [1,2]. However, very limited research was done on investigation of the opposite process of analyte

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